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2. Patent application
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9721215.3

08 OCT 1997

3. Full name, address and postcode of the or of each applicant (underline all surnames)

The Secretary of State for Defence
Defence Evaluation and Research Agency
DERA Farnborough
Farnborough, Hants GU14 OLX

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

54510012

4. Title of the invention

Liquid Crystal Device Alignment

5. Name of your agent (if you have one)

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Description 24

Claim(s) 3

Abstract 1

Drawing(s) 5

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PATENT APPLICATION
LIQUID CRYSTAL DEVICE ALIGNMENT

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Slippery Surfaces cases:

- 1 (P2618)general case.1 - cover all the following file on same day
- 2 (P2619) bistable case - bislip1.doc was pat4 etc involves HP
3. (P2620) twisted nematic tnslipl.doc improves TN devices was pat5 etc
- 25 4 (P2621) ferro electric - feslipl.doc improves FELCDs

LIQUID CRYSTAL DEVICE ALIGNMENT

This invention relates to liquid crystal device alignment.

- 5 Liquid crystal devices typically comprise of a thin layer of a liquid crystal material contained between cell walls or substrates. Optically transparent electrode structures on the walls allow an electric field to be applied across the layer causing a re-ordering of the liquid crystal molecules.
- 10 Many different types of liquid crystal devices are known in the art, for example the twisted nematic device, the cholesteric phase change device, the dynamic scattering device, the supertwisted nematic device and the surface stabilised ferroelectric device modes. It is well known in all of these device modes to provide a surface on the interior walls of the device which will control the alignment of the liquid crystal fluid
- 15 in close proximity to the surface. For many applications of liquid crystal devices, such a treatment is considered necessary in order to impose a particular configuration on the alignment of the liquid crystal fluid throughout the device and/or to provide an optical appearance in the device which is free of apparent optical defects.
- 20 The terms azimuth or azimuthal is used herein to define the molecular (or director \mathbf{n}) alignment angle movement or energy in the plane of the substrate surface. The terms zenith or zenithal is used herein to define the molecular alignment angle movement or energy in a plane normal to the substrate surface.

Several different means are known by which liquid crystal fluids may be aligned on a surface. Evaporation of silicon monoxide from a direction at least 30° from the plane of the substrate provides a surface which aligns a nematic liquid crystal in the plane of the substrate, along an axis orthogonal to the evaporation direction. In contrast, if the evaporation is conducted from a direction making an angle of about 5° or less from the substrate, the resulting surface aligns a nematic liquid crystal along a direction tilted from the plane of the substrate by about 20° in the direction of the evaporation source.

Many commercial liquid crystal devices are fabricated using rubbed polymer alignment layers, especially rubbed polyimide alignment layers. Typically such layers are deposited as an amide precursor polymer by spin deposition of a solution. After removal of the solvent, the polymer coating is imidised by baking at high temperature, then unidirectionally rubbed with a cloth. The resulting surface aligns liquid crystal materials along the direction of rubbing with a tilt out of the plane of the surface in the direction of rubbing. The magnitude of the tilt angle is typically 1° to 2° , but special polyimide formulations and treatments are available which can provide higher magnitudes of pretilt. Some polymer layer are capable of aligning liquid crystal material when cross linked by exposure to linear polarised light (WO95/22075, GB-9444402516). This avoids the need for rubbing which is useful when substrates carry thin film transistors for a part of active matrix displays. The aligned polymer may also be used in conduction with gratings as noted below.

A further means to provide a surface alignment for liquid crystal materials is available from the deposition of different surfactant materials onto the substrate from solution. A range of different surfactants may be used, including quaternary ammonium salts, alkylated silazenes and basic chromium alkanoates. Treatment of the surface usually entails dipping or spin coating with a dilute solution of the surfactant, and usually results in an alignment of the liquid crystal orthogonal to the plane of the substrate, termed homeotropic alignment. Binuclear chromium alkanoates and other binuclear

surfactants may provide alignment in the plane of the substrate without any preferred direction in this plane.

Yet a further method to achieve liquid crystal alignment at a surface involves
5 fabrication of a relief structure such as a relief grating on the surface. Such a structure
may be obtained by photolithographic means, by embossing a compliant surface layer
such as a polymer against a master structure fabricated on, for example, a metal sheet,
by mechanically scribing the surface or by other means. A grating structure aligns a
nematic liquid crystal along the direction of the troughs and crests of the grating. More
10 complex relief structures can provide tilted or bistable alignment.

The alignment methods of the known art suffer a number of shortcomings which
prevent liquid crystal devices manufactured according to these methods from
achieving their full potential utility.

15 One such shortcoming is that it is hardly possible according to known methods, to
provide a surface alignment treatment on which the liquid crystal alignment is free to
adopt any alignment direction in the plane of the surface. A planar alignment may be
obtained by various methods including evaporation of an inorganic material from
20 substantially normal incidence to the substrate, or by coating the substrate with a
known polymer material such as a polyimide material without mechanical rubbing. In
these cases, the alignment of the liquid crystal on the surface is not fixed during the
surface preparation, but is fixed by the alignment of the liquid crystalline phase which
first contacts it, and then becomes immovable.

25 On such a surface the alignment direction is determined by such factors as the flow
direction or the direction of a temperature gradient or electric fields at the time the
liquid crystal phase first contacts the surface. It is desirable to provide a surface
treatment which can allow the liquid crystal alignment direction to rotate freely and
30 repeatedly in the surface plane, but this is not available from known surface
treatments.

A second shortcoming of known liquid crystal alignment techniques is that the energy required to change the zenithal angle between the substrate and the liquid crystal director is much greater than the elastic distortion energy of the liquid crystal itself which is generated by commonly applied voltages. This means that in liquid crystal devices using known alignment techniques, the liquid crystal director remains substantially fixed in tilt angle at the cell walls and the switching of the device which provides an optical effect occurs only in the parts of the device which are separated from the cell walls by some distance which depends on the magnitude of the applied field.

According to this invention the above problems are reduced by a surface alignment treatment which allows movement of liquid crystal molecules at or close to the cell walls, hence the liquid crystal director in contact with the wall to reversibly change its orientation at low values of applied field, for example at applied field strengths of the order of less than 1 volt per micron for an applied electric field. The benefits of such a surface treatment may include reduction in the operating voltage of the device and/or an improvement in the switching behaviour of the device such as the electro-optic threshold steepness of the device which determines the amount of information which may be written on an electro-optic display by means of the known methods of RMS multiplex driving.

According to this invention a liquid crystal device comprises a layer of a liquid crystal material contained between two spaced cell wall carrying electrodes structures and an alignment treatment on at least one wall,

5

Characterised by

means for reducing anchoring energy at the surface alignment on one or both cell walls.

10

The anchoring energy reduced is one or more of: azimuthal anchoring energy, zenithal anchoring energy, and translational anchoring energy (movement along the alignment treated surface).

15 Anchoring energy arises from surface topography eg grooves or gratings, and from chemical bonding interactions. The present invention reduces anchoring energy by changing the chemical bonding. Additionally the surface topography may also be changed, eg to reduce the dimensions of grooves or gratings. The means for reducing energy may be an oligomer or short chain polymer which is either spread on the
20 surface or added to the liquid crystal material. The size of oligomer or short chain polymer may be selected to give a desired amount of preferential deposition at cell walls and slight separation from the liquid crystal material host.

The means for reducing anchoring energy may be an oligomer containing esters,
25 thiols, and/or acrylate monomers and or which is either spread on the surface or added to the liquid crystal material.

The alignment treatment and means for reducing anchoring energy may be provided by a double layer treatment, now referred to as a substrate layer and a polymer layer. The substrate layer may either be formed in the surface of the cell wall, e.g. by

5 mechanical rubbing of the surface, or (and preferably) be a coating on the cell wall.

This coating may include anisotropic features which act to align liquid crystal phases placed in contact with it or in close proximity to it. Such features may include surface relief features including a plain or blazed grating or bibrating structure, or a regular or irregular array of surface features including but not limited to columns, tilted columns,

10 platelets and crystallites e.g. formed by normal or oblique evaporation of inorganic materials onto the surface or by mechanical abrasion or working of the surface. Such features may also include a substantial anisotropy in the substrate formed, for example, by mechanical stretching or rubbing of the substrate layer or by exposure of the substrate layer to polarised actinic radiation.

15

The polymer layer (formed on the substrate layer) has the characteristics of having imperfect solubility in the liquid crystal material used in the device, of having a physical affinity for the surface of the substrate, and of retaining a substantially liquid like surface at the polymer/liquid crystal interface.

20

The polymer may be applied to the device in various ways. In one aspect of the invention, the polymer is formed by polymerisation of reactive low molecular weight materials in solution in the liquid crystal fluid. The resulting solution or dispersion of polymer in liquid crystal is then filled into the cell, and the polymer is allowed to coat

25 the substrate surfaces. Optionally, the dispersion of polymer in liquid crystal may undergo intermediate processes such as filtration or centrifuging prior to being filled into the display cell.

In a further aspect of the invention the reactive low molecular mass materials may be dissolved into the liquid crystal which is then filled into the display cell.

5 Polymerisation is then initiated by known means, such as by heating or exposure to short wavelength optical radiation in the presence of an initiator. After polymerisation the polymer is allowed to diffuse to and coat the substrate layers.

A still further aspect of the invention is provided by polymerisation of the reactive materials in the presence or absence of an inert solvent. The solvent, if present, is
10 removed and the resulting polymer is dissolved in the liquid crystal and filled in to the display cell.

A further aspect of the invention is to form the polymer on the substrate by applying a thin layer of reactive low molecular weight materials to the substrate by known means
15 such as by spinning a stoichiometric amount of each onto the substrate in solution in a solvent. After removal of the solvent, polymerisation is initiated by heating or by exposure to light in the presence of a polymerisation initiator. The treated substrates are then assembled into a cell and the liquid crystal added in.

20 The polymer is characterised in that it is substantially non-crystalline in the presence of the liquid crystal, and that it possesses a glass transition temperature below the operating temperature range of the device. The polymer may be substantially linear in its molecular structure or it may include branch points. The polymer may also be crosslinked to a low degree in order to promote phase separation from the liquid
25 crystal and deposition onto the substrate, but such crosslinking is at such a level that a fluid, gum-like, gel-like or elastic character is retained, and the polymer does not present a hard glassy or solid like character which is retained on heating.

Preferred polymeric materials include thiol/ene polymers prepared by free radical polymerisation of known monomers in the presence of an added thiol compound which serves to limit the molecular weight of the product through chain transfer reactions. Details of suitable material are listed later.

The invention will now be described, by way of example only, with reference to the accompanying drawings in which:-

10 Figure 1 is a plan view of a matrix multiplexed addressed liquid crystal display;

Figure 2 is the cross section of the display of figure 1;

Figure 3 shows the configuration for photolithographic exposure leading to the formation of an asymmetric monograting useful in twisted nematic devices.

Figure 4 shows the transmission versus voltage data for two twisted nematic cells, one of which (dotted line) has been treated with an additive (Norland 65) to give weak anchoring on asymmetric gratings.

20

Figure 5 shows the optical contrast ratio versus voltage data for two twisted cells, one of which (dotted line) has been treated with an additive to give weak anchoring.

Figure 6 shows transmission - voltage curves for two voltage controlled twist type cells, one with a standard alignment, the other with a weak anchoring energy treatment.

25

Figure 7 shows the configuration for photolithographic exposure leading to the formation of a bigrating with orthogonal grating modulations.

30

Figure 8 shows switching characteristics for two bistable cells. one with standard alignment. the other with a weak surface anchoring energy.

Figure 9 shows diagrammatically a smectic liquid crystal molecule. and how it moves
5 within a layer when switched to its bistable states in a ferroelectric liquid crystal cell.

Figure 10 shows variation in memory angle against applied voltage for two bistable ferroelectric liquid crystal devices, one with standard alignment. the other with a weak surface anchoring energy.

Examples of devices: twisted nematic type device.

The display in figures 1, 2 comprises a liquid crystal cell 1 formed by a layer 2 of
5 nematic or long pitch cholesteric liquid crystal material contained between glass walls
3, 4. A spacer ring 5 maintains the walls typically 2-10 μ m apart. Additionally
numerous beads of the same dimensions may be dispersed within the liquid crystal to
maintain an accurate wall spacing. Strip like row electrodes 6 e.g. of SnO₂ or ITO are
formed on one wall 3 and similar column electrodes 7 are formed on the other wall 4.
10 With m-row and n-column electrodes this forms an m \times n matrix of addressable
elements or pixels. Each pixel is formed by the intersection of a row and column
electrode. A row driver 8 supplies voltage to each row electrode 6. Similarly a column
driver 9 supplies voltages to each column electrode 7. Control of applied voltages is
from a control logic 10 which receives power from a voltage source 11 and timing
15 from a clock 12.

Either side of the cell 1 are polarisers 13, 13' arranged with their polarisation axis
substantially crossed with respect to one another. An additional optical compensator
such as a stretched plastic film may also be added between the liquid crystal cell and
one of the polarisers. A partly reflecting mirror 16 may be arranged behind the cell 1
20 together with a light source 15. These allow the display to be seen in reflection and lit
from behind in dull ambient lighting. For a transmission device, the mirror may be
omitted.

25 Prior to assembly, the cell walls 3, 4 are treated with alignment treatments to provide a
monostable pretilted alignment. The alignment directions R1, R2 are shown as
orthogonal to give a 90° or 270° twisted cell, but may be at other angles, e.g. at 45°.
Finally the cell is filled with a nematic material which may be e.g. E7, ZLI2293 or
MLC 6608 (Merck), and may include a chiral additive such as CB15 or R1011
30 (Merck).

In use the display may be multiplex addressed in a conventional manner by the application of a row waveform applied to each row in turn whilst applying waveforms to all columns. Such addressing is capable of applying two different rms value waveforms at each x,y intersection. One waveform has an rms value above a switching threshold and will therefore switch the liquid crystal material to an ON state. The other resultant waveform has an rms value below the switching threshold and therefore does not switch the liquid crystal material.

10 The number of x,y pixel elements that can be rms addressed is limited by the steepness of a device transmission verses voltage curve (as described by Alt and Pleshko in IEEE Trans ED vol ED 21, (1974) P.146 - 155). Therefore improvements to the steepness of the transmission - voltage curve is highly desirable. Additionally, if more of the material can be switched (switching the molecules adjacent a wall surface, rather than switching only at the layer centre) then a higher contrast between ON and OFF states would be obtained.

One example of a weak anchoring surface treatment for improving a twisted nematic device uses asymmetric monograting surfaces similar to those described in GB
20 9402492.4 P2246 GB-A-2.296.466. WO-95/22078.

The asymmetric monogratings used to induce pretilted alignment are fabricated in the following way, as in Figure 3. Shipley 1805 photoresist 20 was spin coated at 3000 rpm onto ITO coated glass 21 for 30 seconds. Next the photoresist layer 20 was baked at 90°C for 30 minutes to remove the solvent. Exposure of the photoresist through a mask 22 was carried out using off axis hard contact photolithography at an incident angle of 60° as shown in Figure 3. The mask 22 consisted of a chrome on glass pattern with a pitch of 1µm (0.5µm gaps and 0.5µm chrome strips). The exposure time was set to 540 seconds with an incident power of 0.15 mW/cm² from a mercury lamp.

30 Development was then carried out in Shipley MF319 for 10 s followed by a water

rinse. Samples were finally baked at 160°C for 45 minutes after first receiving a deep UV exposure to preharden the photoresist 20 (3.36 J/cm² at 254nm).

The above process resulted in a surface monograting with a 1µm pitch and a 0.5µm
5 peak to trough groove depth. The profile is asymmetric which leads to a pretilted alignment if the nematic is under the influence of a bulk twist torque (see GB 9402492.4). These surfaces were constructed into cells in which the groove direction R1, on one surface was orthogonal to the groove direction R2 on the other. The cell gap was set to 2.05µm which corresponds to the first Gooch and Tarry minimum when
10 used with E7 (J. Phys. D. Appl. Phys. vol. 8, p. 1575 (1975)). Filling was then carried out using E7 in the isotropic phase (65°C) followed by slow cooling to room temperature. Such a cell gives a strong surface anchoring as noted below.

A second cell was made as above, but incorporating 2% of N65 in E7. The N65/E7
15 mixture was cured for 10 minutes by exposure to unfiltered mercury lamp with an optical output of 2.0mW/cm² in a fused silica cell prior to filling in the cell. N65 is a UV curing adhesive manufactured by Norland Products Inc., North Brunswick NJ, USA; other similar materials are N63, N60, N123. The materials contain a mixture of esters and acrylate monomers which polymerise under UV radiation. Such a cell gives
20 a weak surface anchoring as noted below.

The electrooptic response of cells containing different N65/E7 mixtures was the recorded by placing the twisted nematic cell between crossed polarisers 13, 13' which were oriented parallel to the adjacent grating alignment directions R1, R2..
25 Transmission was measured using a photodiode with a photopic response during the application of a 1kHz sinusoidal drive waveform. Figure 4 shows the transmission versus rms voltage for two cells one containing E7 (strong surface anchoring) and the other cell containing 2% of N65 in E7 and cured as above (weak surface anchoring). The data clearly shows that the weak anchoring treatment has lowered the operating
30 voltage. A transmission of 50% of the zero volt value is reached at a voltage of 1.83 V for the weak anchored surface and 2.13 V for the strong anchored surface. The power

consumption of a display can be considered in the most simple case as the power required to charge and discharge a capacitor which is proportional to V^2 . Therefore the weak anchored surface is expected to allow a power saving of roughly 35%.

- 5 The second improvement of the weak anchored cell is the improved optical contrast ratio as shown in Figure 5. At 5 V the weak anchored cell has a contrast ratio of 126 while the strong anchored cell has a contrast ratio of 49. At 8 V the difference is even larger (410 and 74 respectively). Therefore if a particular application demands a certain contrast ratio then it can be reached at a much lower voltage with a weak
10 anchored surface. The weak anchoring has also lead to a significant improvement in the steepness of the electrooptic response. For the weak anchored surface $V_{90} - V_{50}$ is 0.454 V while for the strong surface this quantity is 0.510 V.

In summary the above experimental results show that a surface which has been treated
15 to give a lower zenithal anchoring energy (W_θ) can improve a twisted nematic device. The improvements include a lower voltage threshold, a steeper electro optic response and a higher optical contrast.

The above improvements may also be applied to other twisted nematic displays. For
20 example dyed displays where an amount of a dye is incorporated into the liquid crystal material. Such dyed displays may be operated with one or two polarisers. One suitable dye is D102 (Merck material) present in up to about 5% typically 2%.

Another nematic display uses parallel alignment directions on the two cell walls, with
25 or without an amount of pleochroic dye. Such a device operates as a switchable birefringent element.

Example of devices: voltage controlled twist (VCT) device.

An alternative twisted nematic device is one which is switched from a non-twisted state at zero volts to a twisted state at a higher voltage as described in GB 9607854.8 PCT/GB97/01019 which will be referred to as a voltage controlled twist (VCT) device. Operation of the VCT device may be improved by the addition of a weak
5 anchoring treatment. The surface alignment in this example was provided by asymmetric grating surfaces as described above for the twisted nematic device, and as in GB-A-2,296,466, WO-95/22078.

The weak anchoring treatment was MXM035 (a two component Merck material)
10 mixed from 10 % of part A and 90% of part B. 4% of this mixture was added to nematic MLC 6608 (a Merck material) which has a negative dielectric anisotropy. The MXM035 was then cured by placing the MXM035/MLC6608 mixture in a glass cell and exposing to UV radiation (10 minutes at 2.0mW/cm² while at a temperature of 65°C). After curing the mixture was used to fill a VCT test cell.

15 The VCT cells were constructed as in Figure 2 so that the grating grooves on one surface were orthogonal to those on the other. Prior to construction the grating on one surface was treated with a chrome complex surfactant in order to induce a homeotropic boundary condition (molecules perpendicular to the wall surface). The grating on the
20 other surface was left untreated in order to induce a planar boundary condition. The cell gap was set to 5.3µm using spacer beads in the edge seal. Figure 6 shows the electrooptic response of two VCT devices, one of which contains the weak anchoring treatment. The VCT containing pure MLC6608 exhibits 50% transmission at a voltage of 2.91 V while the VCT containing 4% MXM035 in MLC 6608 exhibits 50%
25 transmission at a voltage of 1.52 V. Therefore the weak anchoring treatment has lead to a dramatic decrease in operating voltage.

The dynamic response of the VCT were measured for these cells for switching between 0 V and 5V as shown in table 3. It can be seen that the addition of MXM035 has lead to a decrease in switch-on time (τ_{on}) and an increase in switch-off time (τ_{off}).

Cell Mixture	τ_{on} (ms)	τ_{off} (ms)
MSc 6608	86	60
MSC 6608 + 4%MXM035	60	112

Table 3; 0-5 V optical switching times for VCT cells with strong or weak anchoring.

Examples of devices: bistable nematic device

- One bistable nematic device is described in GB.2,286,467-A. This uses accurately formed bigratings on at least one cell wall. The bigrating permits liquid crystal molecules to adopt two different angular aligned directions when suitable electrical signals are applied to cell electrodes, e.g. dc coupling to flexoelectric polarisation as described in Patent Application No. WO.92/00546. Since in the two splayed states the director is quite close to being in the plane of the layer, the coupling between director and flexoelectric component can be small, which may hinder switching in some circumstances.

The bistable nematic device of GB2286467-A also has a further problem which is not present in ferroelectric devices, that is, the need to switch the surface layer of molecules in order to eliminate image sticking effects. Surface layer switching usually requires high voltages in order to overcome the inelastic memory anchoring (P. Vetter et al. EuroDisplay 1993, SID, p.9) which is due to microscopic absorption of the first nematic layer into the surface.

The present invention improves the switching of the bistable nematic device described in GB2286467-A, by reducing or eliminating surface sticking effects.

A weak anchoring treatment can be added to the bistable nematic device to produce a surface which induces a planar alignment or tilted planar alignment and furthermore has a degenerate azimuthal anchoring energy ($W_\phi=0$) combined with a reduced
5 zenithal anchoring energy (W_θ). This leads to lower voltage operation. To show the effect of reduced anchoring energy, a cell having two bigratings with zero pretilt was constructed as follows.

Figure 7 shows an arrangement as in GB-A-2.286.467, with a substrate 21 covered by
10 a photo resist layer 20, and a mask 22. Samples were made by spin coating 1805 photoresist 20' onto ITO coated glass 21' at a spin speed of 3000 rpm to give a coating thickness of $0.55\mu\text{m}$. The samples were then softbaked at 90°C for 30 minutes. The bigrating was exposed using hard contact photolithography through a mask 22' with a typical exposure time of 250s (at 0.3 mW/cm^2) at normal incidence, not the 60° shown
15 in Figure 7. The mask 22' contained a bigrating pattern with a pitch of $1.4\times 1.4\mu\text{m}$ ($0.9\mu\text{m}$ chrome squares separated by $0.5\mu\text{m}$ gaps in each direction). Development was then carried out in Shipley MF319 for 10 s followed by a water rinse. Samples were finally baked at 160°C for 45 minutes after first receiving a deep UV exposure to
20 preharden the photoresist (3.36 J/cm^2 at 254nm). This process created a bigrating with two identical modulations each of which had a symmetric profile. The alignment of a nematic on this consists of two non tilted alignment states separated by an azimuthal angle of 90° .

Cells were then made with these zero pretilt bigratings on both inner surfaces arranged
25 so that the groove directions on one surface coincided with the groove directions on the other. These were filled with E7 nematic containing various concentrations of N65. On cooling to room temperature all cells showed two alignment directions. As the states have no pretilt there is no method by which only one state can be selected using applied electrical pulses. However random switching between the states can occur
30 which was seen by pulse-induced domain wall movement. Rectangular monopolar

pulses of various pulse lengths were applied to each cell. Each pulse alternated in sign from the previous pulse to maintain a dc balance. Pulses were separated by a time interval 100 times the pulse length. For each pulse length a voltage existed above which domain wall movement occurred. Figure 8 shows this threshold voltage versus time for two cells. The cell gaps were set to $0.95\mu\text{m}$. The figure compares data from a cell filled with pure E7 to that taken from a cell filled with a 2% precured mixture of N65 in E7. The N65 has clearly lowered the voltage threshold to a value of only $5.0\text{ V}/\mu\text{m}$ for a 10.8 ms pulse. In contrast the pure E7 cell shows a much higher voltage switching ($15.0\text{ V}/\mu\text{m}$) and in fact suffered dielectric breakdown for low pulse lengths.

The above results show that the N65 treatment leads to a low voltage bistable switching which is consistent with a low zenithal anchoring energy combined with no in-plane memory anchoring other than the elastic W_ϕ imposed by the bigrating.

For actual display devices, it is necessary to use alignment with some pretilt. In order to obtain fully selective bistable switching one state has to be favoured by the applied pulse. This can be achieved using dc coupling to a flexoelectric polarisation if the two bistable states have the appropriate pretilts. The device described in GB2286467-A achieves pretilt by using a bigrating in which both modulations have asymmetric profiles. This method allows a pretilt of typically 17° for one of the bistable states while maintaining a pretilt of 0° for the other state. These surfaces were tested in conjunction with the N65 treatment using the following fabrication process as illustrated in Figure 7.

A thin layer 20 of 1805 was spun onto ITO coated glass 21 as described above. After softbaking, the layer 20 was exposed through the $1.4 \times 1.4\mu\text{m}$ mask using an off axis diagonal exposure geometry as shown in Figure 7; i.e. exposure at about 60° to the surface normal and about 45° to the mask array of square pixels. The exposure time was set to 540 seconds (at $0.15\text{ mW}/\text{cm}^2$). After development and processing the

bigrating was constructed opposite a flat photoresist surface (i.e. no grating and hence

zero pretilt) using $10\mu\text{m}$ cell spacers to allow measurement of the surface pretilt at the bigrating surface.

The amount of pretilt depends upon the amount of e.g. N65 incorporated in the
5 nematic host. For an appropriate amount of N65, the pretilt can be close to a cell
having nematic E7 only. For example a cell with E7 only has been measured to have a
pretilt of about 17.5° ; 2%N65 precured in E7 mixed with pure E7 (1:1 ratio), was
found to have a pretilt of 17.1° .

10 Bistable devices with bigratings as above may be incorporated into display devices as
shown in Figures 1, 2, with alignment directions as indicated by R1 and R2.

Examples of devices: ferroelectric device.

15 Smectic liquid crystal devices can be made as in Figures 1, 2 but with a layer of
smectic liquid crystal material and with parallel or antiparallel alignment directions
R1, R2.

If the smectic material is a chiral smectic e.g. smectic C (S_C^*) then a bistable device
20 can be made. Such a device is the surface stabilised ferroelectric device supporting
two bistable states which are optically distinct (see N. A. Clark and S. T. Lagerwall,
Appl. Phys. Lett., **36**, 899 (1980)). In a chiral smectic material molecules tend to lie
and move along the surface of an (imaginary) cone as shown in Figure 9. When the
surface alignment directions R1, R2 are parallel the (z) axis of these cones are parallel
25 to these alignment directions and the molecules lie either side of the axis on the cone
surface. In one switched state D1 the molecules lie on one side of the cone, and in the
second bistable state D2 lie on the other side of the cone. The switching is achieved
by application of a voltage pulse of appropriate sign and length applied through the
electrodes 6, 7 coupling with a spontaneous polarisation coefficient of the material.
30 The cone angle, θ_c , is a function of material parameters. In devices the molecules in
their two switched positions D1, D2, do not lie on the extremities of the cone but some

small distance away. This means that the angle between the bistable positions is somewhat less than the cone angle, and can be increased a bit by application of an ac voltage signal to the material; this is known as ac stabilisation. Ideally the angle between the switched states is 45° because this would allow maximum contrast for the cell when arranged between crossed polarisers with the axis of one polariser along one of the switched directions. This gives a dark state in one switched position and a light state in the other switched position. The angular distance between the two state is defined as the memory angle, θ_m (see N. Itoh et al, Jpn. J. Appl. Phys., **31**, L1089 (1992)). The optimum memory angle for maximum brightness in the light state is therefore 45° . However most materials possess a memory angle which is much less than 45° and so suffer from loss in brightness.

A weak anchoring treatment can be added to a ferroelectric to increase the memory angle and so improve the display brightness. This treatment also allows small amounts of translational movement of micro layers formed during cooling from isotropic phases to smectic phases leading to improve alignment etc.

Alignment surfaces were prepared by spin coating a layer of probomide 32 (Ciba Geigy) onto ITO coated glass and baking the substrates at 300°C . The surfaces were then rubbed in one direction by a nylon cloth attached to a rotating roller. Finally cells were constructed in which the rubbing direction on one surface was parallel to that on the other. The cell gap was set to $1.1\mu\text{m}$ using monodispersed spacer beads in the edge seal. Each cell was then filled with ZLI 5014 (Merck) ferroelectric liquid crystal doped with small percentages of N65. Before filling the N65 was cured in a separate cell.

25

Figure 10 shows the memory angle measured from two cells containing either pure ZLI 5014, or ZLI....., or 4% N65 in ZLI 5014 as a function of applied voltage (50kHz AC). The results clearly show that the weak anchoring treatment has lead to a significant increase in memory angle at all voltages. Therefore the treatment has improved this ferroelectric device by increasing the on state transmission between

30

crossed polarisers. For example at 5 V, the memory angle has increased from 17.1° to 34.4° which would lead to a device which is 3.7 times brighter.

Bistable ferro electric devices switch upon receipt of a unidirectional pulse of
5 appropriate direction, amplitude, and length. This contrasts with switching upon
receipt of a suitable rms signal as with twisted nematic devices. The arrangement of
Figure 1 can be used for FELCD using strobe pulses applied sequentially down the
rows, whilst one of two different data pulses are applied to each column. Examples of
addressing are described in GB 2,232,802B, USP-5,497,173, WO89/05025, EP-
10 0391931, WO91/02925, GB-2,262831,

Several other smectic devices may be made with alignment surfaces of the present
invention. For examples electro-clinic smectic devices; mono stable ferro electric
devices USP-4,969,719, GB-2,210,0468, USP-4,997,264. GB-2,210,469, USP-
15 5,061,047, GB-2,209,610B colour change smectic projection cells USP-5,189,534,
GB-2,236,403. The alignment may produce a chevron type C1 or C2 type of smectic
micro layer arrangement; or a tilted bookshelf arrangement where rubbing directions
on opposite walls are in the same direction, or real bookshelf alignment.

The monomer materials used may include the following, which are given only by way of example:

methyl acrylate	propane-1,3-diol diacrylate
ethyl acrylate	butane-1,4-diol diacrylate
propyl acrylate	pentane-1,5-diol diacrylate
butyl acrylate	hexane-1,6-diol diacrylate
pentyl acrylate	heptane-1,7-diol diacrylate
2-methylbutyl acrylate	octane-1,8-diol diacrylate
hexyl acrylate	nonane-1,9-diol diacrylate
heptyl acrylate	decane-1,10-diol diacrylate
octyl acrylate	glycerol triacrylate
nonyl acrylate	trimethylolpropane triacrylate
decyl acrylate	pentaerythritol triacrylate
ethyl hexyl acrylate	pentaerythritol tetraacrylate
methyl methacrylate	di-pentaerythritol hexaacrylate
ethyl methacrylate	ethylene glycol dimethacrylate
propyl methacrylate	1,2-propylene glycol dimethacrylate
butyl methacrylate	propane-1,3-diol dimethacrylate
pentyl methacrylate	butane-1,4-diol dimethacrylate
2-methylbutyl methacrylate	pentane-1,5-diol dimethacrylate
hexyl methacrylate	hexane-1,6-diol dimethacrylate
heptyl methacrylate	heptane-1,7-diol dimethacrylate
octyl methacrylate	octane-1,8-diol dimethacrylate
nonyl methacrylate	nonane-1,9-diol dimethacrylate
decyl methacrylate	decane-1,10-diol dimethacrylate
ethyl hexyl methacrylate	glycerol trimethacrylate
styrene	trimethylolpropane trimethacrylate
ethylene glycol diacrylate	pentaerythritol trimethacrylate
1,2-propylene glycol diacrylate	pentaerythritol tetramethacrylate
	di-pentaerythritol hexamethacrylate

A further class of polymers includes di-thiol/diene polymers prepared by the copolymerisation of difunctional alkenes with difunctional thiols under free radical conditions. Monofunctional and/or polyfunctional alkenes and/or thiols may be incorporated in order to modify the properties of the polymer. for example to reduce
5 the molecular weight of the polymer or to introduce a controlled degree of crosslinking in the polymer. The following materials given by way of example only may be included in polymers suitable for the subject of the invention:

methyl acrylate
ethyl acrylate
propyl acrylate
butyl acrylate
pentyl acrylate
2-methylbutyl acrylate
hexyl acrylate
heptyl acrylate
octyl acrylate
nonyl acrylate
decyl acrylate
ethyl hexyl acrylate
methyl methacrylate
ethyl methacrylate
propyl methacrylate
butyl methacrylate
pentyl methacrylate
2-methylbutyl methacrylate
hexyl methacrylate
heptyl methacrylate
octyl methacrylate
nonyl methacrylate
decyl methacrylate

styrene
ethylene glycol diacrylate
1,2-propylene glycol diacrylate
propane-1,3-diol diacrylate
butane-1,4-diol diacrylate
pentane-1,5-diol diacrylate
hexane-1,6-diol diacrylate
heptane-1,7-diol diacrylate
octane-1,8-diol diacrylate
nonane-1,9-diol diacrylate
decane-1,10-diol diacrylate
glycerol triacrylate
trimethylolpropane triacrylate
pentaerythritol triacrylate
pentaerythritol tetraacrylate
di-pentaerythritol hexaacrylate
ethylene glycol dimethacrylate
1,2-propylene glycol dimethacrylate
propane-1,3-diol dimethacrylate
butane-1,4-diol dimethacrylate
pentane-1,5-diol dimethacrylate
hexane-1,6-diol dimethacrylate
heptane-1,7-diol dimethacrylate

ethyl hexyl methacrylate
ethylene glycol divinyl ether
1,2-propylene glycol divinyl ether
propane-1,3-diol divinyl ether
butane-1,4-diol divinyl ether
pentane-1,5-diol divinyl ether
hexane-1,6-diol divinyl ether
heptane-1,7-diol divinyl ether
octane-1,8-diol divinyl ether
nonane-1,9-diol divinyl ether
decane-1,10-diol divinyl ether
glycerol trivinyl ether
trimethylolpropane trivinyl ether
divinyl benzene
butane-1,3-diene
pentane-1,4-diene
hexane-1,5-diene
heptane-1,7-diene
octane-1,7-diene
nonane-1,8-diene
decane-1,9-diene
ethylene glycol dithioglycollate
1,2-propylene glycol dithioglycollate
propane-1,3-diol dithioglycollate
butane-1,4-diol dithioglycollate
pentane-1,5-diol dithioglycollate
hexane-1,6-diol dithioglycollate
heptane-1,7-diol dithioglycollate
octane-1,8-diol dithioglycollate
nonane-1,9-diol dithioglycollate
decane-1,10-diol dithioglycollate

octane-1,8-diol dimethacrylate
nonane-1,9-diol dimethacrylate
decane-1,10-diol dimethacrylate
glycerol trimethacrylate
trimethylolpropane trimethacrylate
pentaerythritol trimethacrylate
pentaerythritol tetramethacrylate
di-pentaerythritol hexamethacrylate
ethylene glycol diallyl ether
1,2-propylene glycol diallyl ether
propane-1,3-diol diallyl ether
butane-1,4-diol diallyl ether
pentane-1,5-diol diallyl ether
hexane-1,6-diol diallyl ether
heptane-1,7-diol diallyl ether
octane-1,8-diol diallyl ether
nonane-1,9-diol diallyl ether
decane-1,10-diol diallyl ether
glycerol triallyl ether
trimethylolpropane triallyl ether
di-allyl malonate
di-allyl succinate
di-allyl glutamate
di-allyl hexane-1,6-dicarboxylate
di-allyl heptane-1,7-dicarboxylate
di-allyl octane-1,8-dicarboxylate
di-allyl nonane-1,9-dicarboxylate
di-allyl decane-1,10-dicarboxylate
di-allyl undecane-1,11-dicarboxylate
di-allyl dodecane-1,12-dicarboxylate
di-allyl phthalate

glycerol trithioglycollate
trimethylolpropane trithioglycollate
pentaerythritol trithioglycollate
pentaerythritol tetrathioglycollate
di-pentaerythritol hexathioglycollate
4,4'-thiobisbenzenethiol
di-allyl iso-phthalate
di-allyl terephthalate
ethane dithiol
propane dithiol
butane dithiol
pentane dithiol

hexane dithiol

heptane dithiol
octane dithiol
nonane dithiol
decane dithiol
undecane dithiol
dodecane dithiol
ethylene glycol di-3-
mercaptopropionate
1,2-propylene glycol di-3-
mercaptopropionate
propane-1,3-diol di-3-
mercaptopropionate

butane-1,4-diol di-3-mercaptopropionate
pentane-1,5-diol di-3-mercaptopropionate
hexane-1,6-diol di-3-mercaptopropionate
heptane-1,7-diol di-3-mercaptopropionate
octane-1,8-diol di-3-mercaptopropionate
nonane-1,9-diol di-3-mercaptopropionate
decane-1,10-diol di-3-mercaptopropionate
glycerol tri-3-mercaptopropionate
trimethylolpropane tri-3-mercaptopropionate
pentaerythritol tri-3-mercaptopropionate
pentaerythritol tetra-3-mercaptopropionate
di-pentaerythritol hexa-3-
mercaptopropionate

Also commercial polymers from Norland
and Merck eg Norland 65. Norland 63 and
Merck MXM035

Claims:

1. A liquid crystal device comprises a layer of a liquid crystal material contained between two spaced cell wall carrying electrodes structures and an alignment treatment
5 on at least one wall,

characterised by

means for reducing anchoring energy at the surface alignment on one or both cell
10 walls.

2. The device of claim 1 wherein the means for reducing energy is an oligomer or short chain polymer within the liquid crystal material at the cell walls.

15 3. The device of claim 1 wherein the means for reducing energy is an oligomer containing esters, thiols, and/or acrylate monomers within the liquid crystal material at the cell walls.

4. The device of claim 2 wherein the oligomer or short chain polymer has imperfect
20 solubility in the liquid crystal material.

5. The device of claim 2 wherein the oligomer or short chain polymer has a physical affinity for the surface of the cell wall.

25 6. The device of claim 2 wherein the oligomer or short chain polymer retains a substantially liquid like surface at the polymer and liquid crystal material interface

7. The device of claim 2 wherein the oligomer or polymer is substantially non-crystalline within the liquid crystal material.

8. The device of claim 2 wherein the oligomer or polymer reduces the liquid crystal material order parameter at or adjacent the cell walls.
- 5 9. The device of claim 2 wherein the oligomer or polymer changes the phase of the liquid crystal material at or adjacent the cell walls.
10. The device of claim 2 wherein the oligomer or polymer has a glass transition temperature below the operating temperature range of the device.
- 10 11. The device of claim 2 wherein the oligomer or polymer is substantially linear or includes branch points, either with or without crosslinking.
12. The device of claim 2 wherein the oligomer or polymer has a number of repeat
15 units within the range of 4 to 1000.
13. A method of making a liquid crystal device comprising the steps of:-
- providing a layer of a liquid crystal material contained between two spaced cell wall
20 carrying electrodes structures and an alignment treatment on at least one wall.
- characterised by
- the step of reducing anchoring energy at the surface alignment on one or both cell
25 walls.
14. The method of claim 11 wherein the oligomer or short chain polymer is formed by polymerisation of reactive low molecular weight materials in solution in the liquid crystal fluid.

15. The method of claim 11 wherein the oligomer or short chain polymer is formed by polymerisation of reactive low molecular weight materials in solution in the liquid crystal material prior to its introduction between the cell walls.

5

16. The method of claim 11 wherein the oligomer or short chain polymer is formed by polymerisation of reactive low molecular weight materials in solution in the liquid crystal material after to its introduction between the cell walls.

10 17. The method of claim 11 wherein the oligomer or short chain polymer is formed by polymerisation of reactive low molecular weight materials in the presence of an inert solvent which is then removed and the resulting polymer dissolved in the liquid crystal material prior to its introduction between the cell walls.

Abstract.

5 Liquid crystal devices are formed by a layer of a liquid crystal material enclosed
between two cell walls, both carrying electrode structures, and one or both walls
treated to align molecules of the liquid crystal material. Most alignment treatment
give alignment and surface pretilt with a strong azimuthal and zenithal anchoring
energy to contacting liquid crystal molecules. The invention reduces at least one of
10 the azimuthal zenithal or translational anchoring energy to improve switching
characteristics and optical performance by allowing movement of liquid crystal
molecules at or close to the cell wall. The reduction of anchoring energy may be
achieved by an oligomer or short chain polymer which is either spread on the surface
or added to the liquid crystal material. The size of oligomer or short chain polymer is
15 low enough that it does not appreciably phase separate from the liquid crystal material.
The polymer layer has the characteristics of having imperfect solubility in the liquid
crystal material used in the device, of having a physical affinity for the surface of the
substrate, and of retaining a substantially liquid like surface at the polymer/liquid
crystal interface. The polymer may be formed by polymerisation of reactive low
20 molecular weight materials in solution in the liquid crystal fluid. The resulting solution
or dispersion of polymer in liquid crystal is then filled into the cell, and the polymer is
allowed to coat the substrate surfaces.



Fig.1.

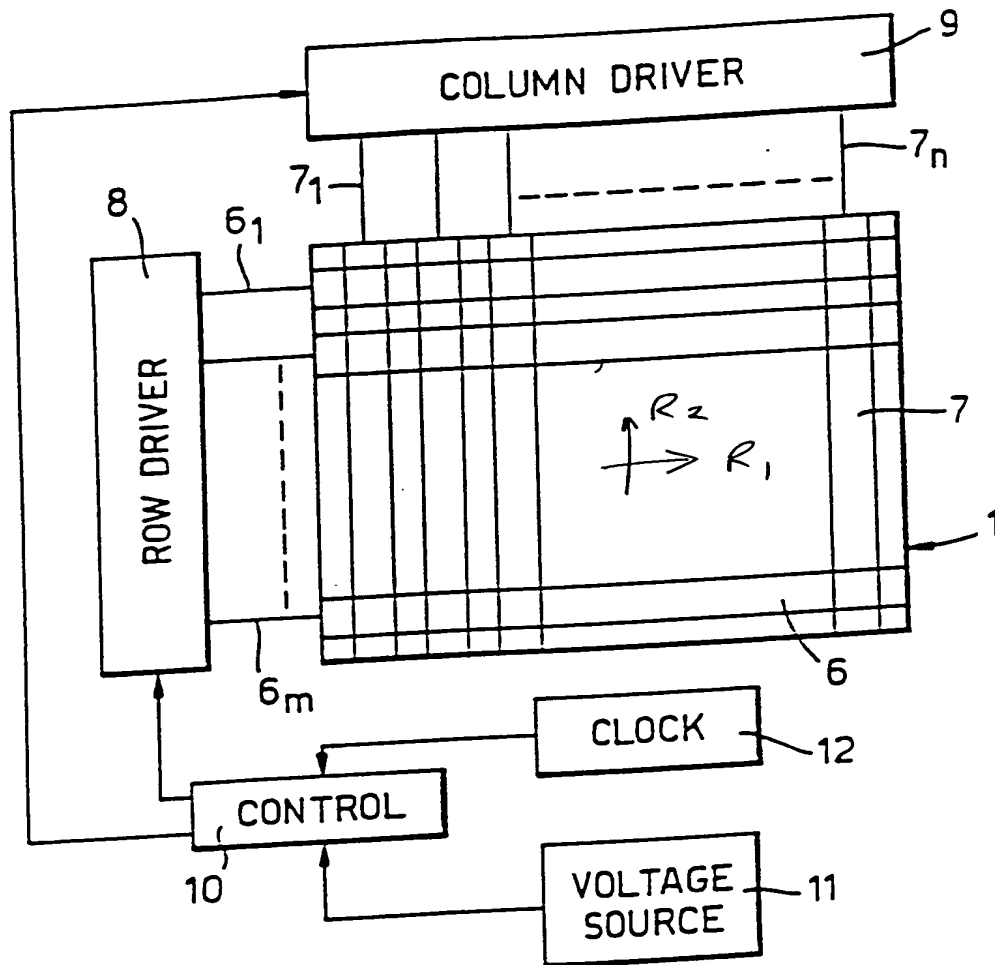


Fig.2.

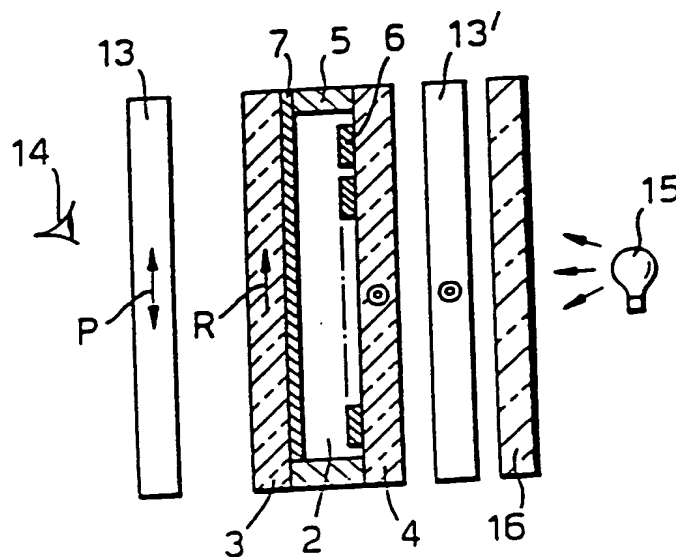




Figure 3 mono grating

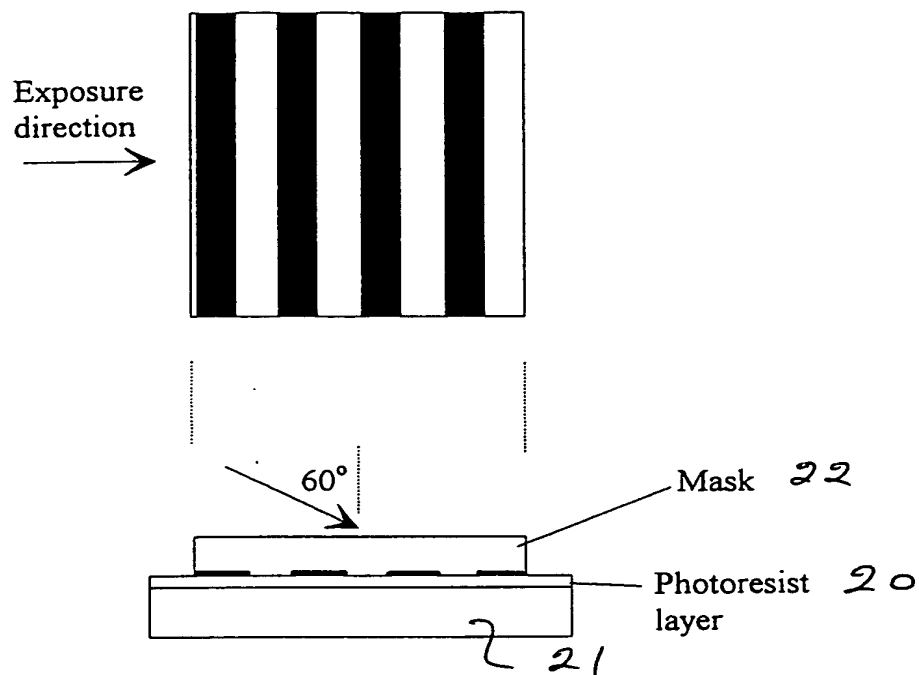


Figure 4 TN

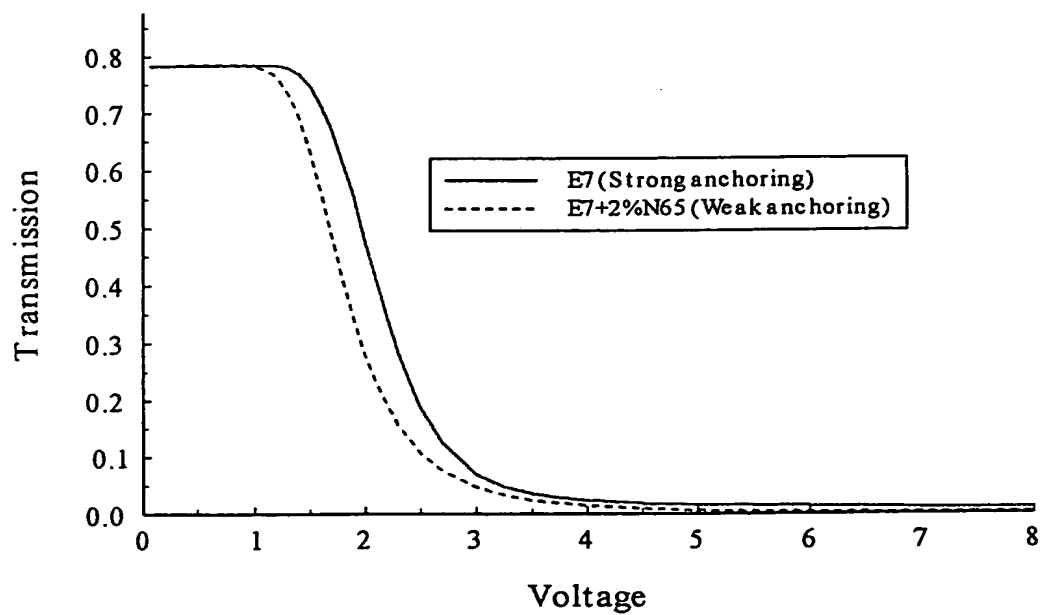




Figure 5 TN

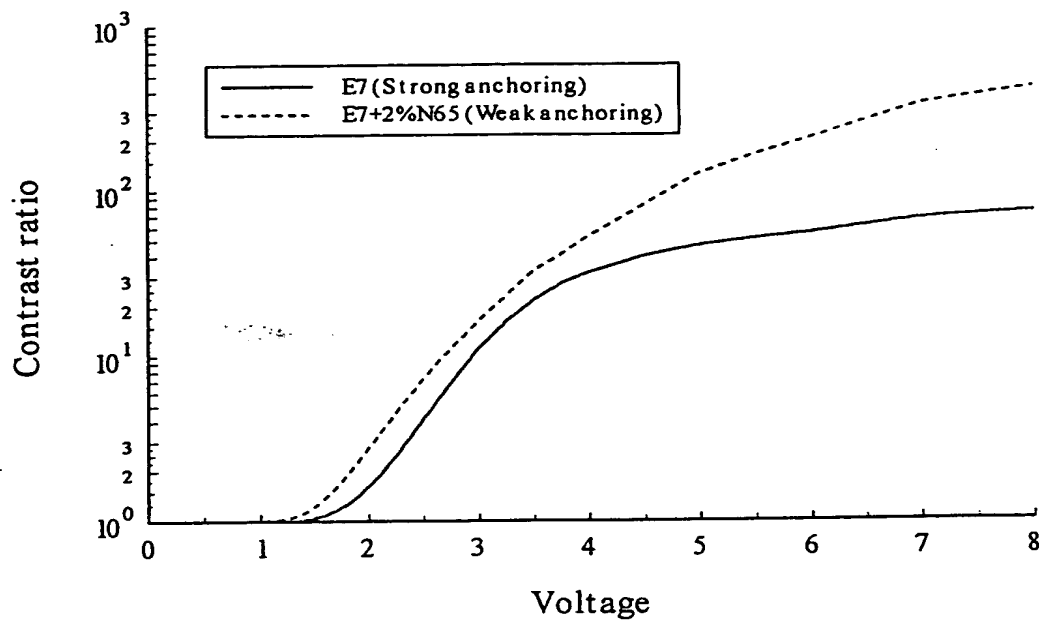
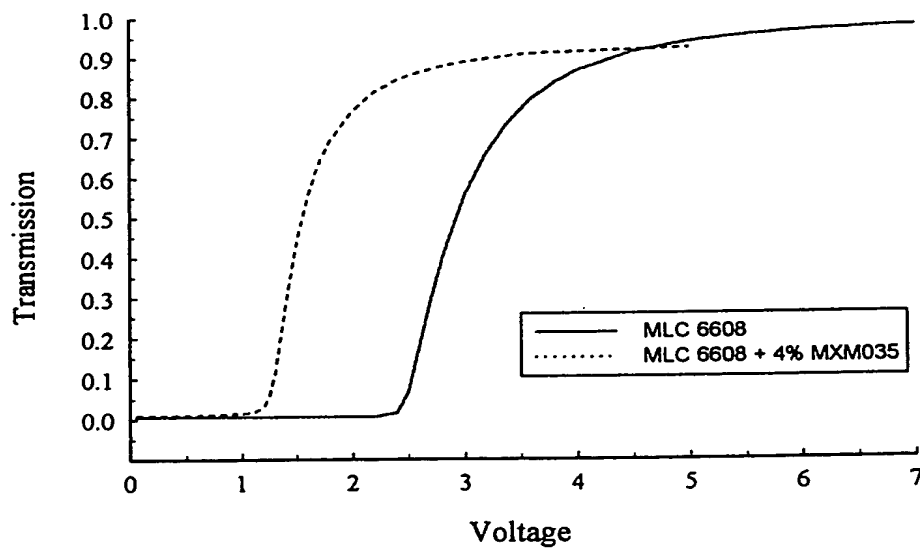


Figure 6 VCT





4/5

Figure 7 bigrating mask

Exposure
direction

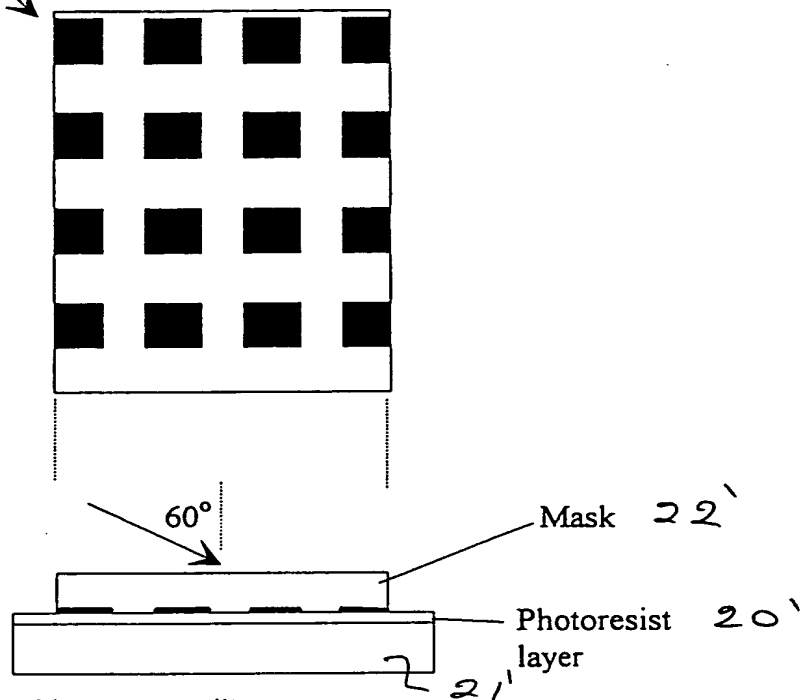


Figure 8 bi stable with zero pretilt

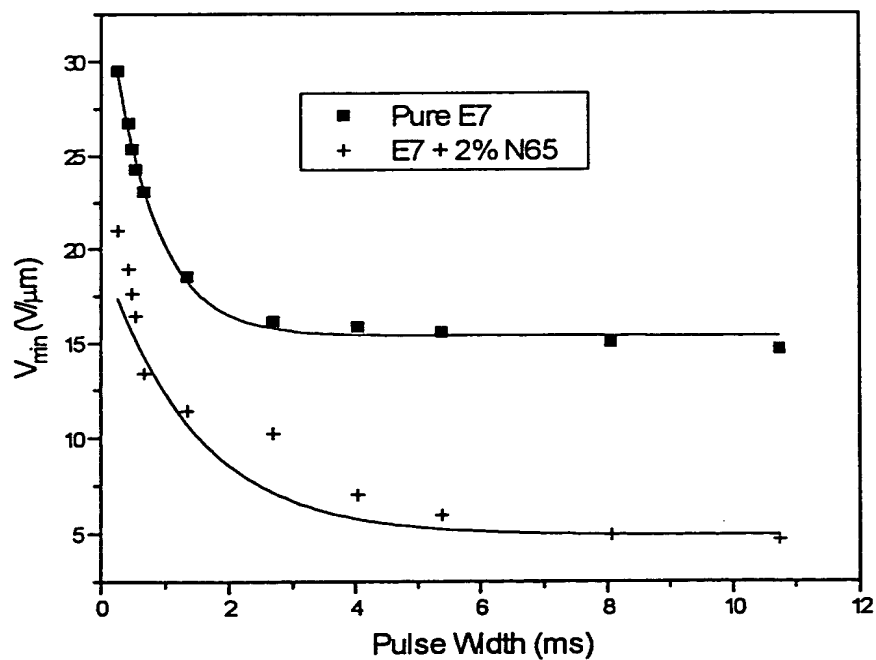




Figure 9 FE cone

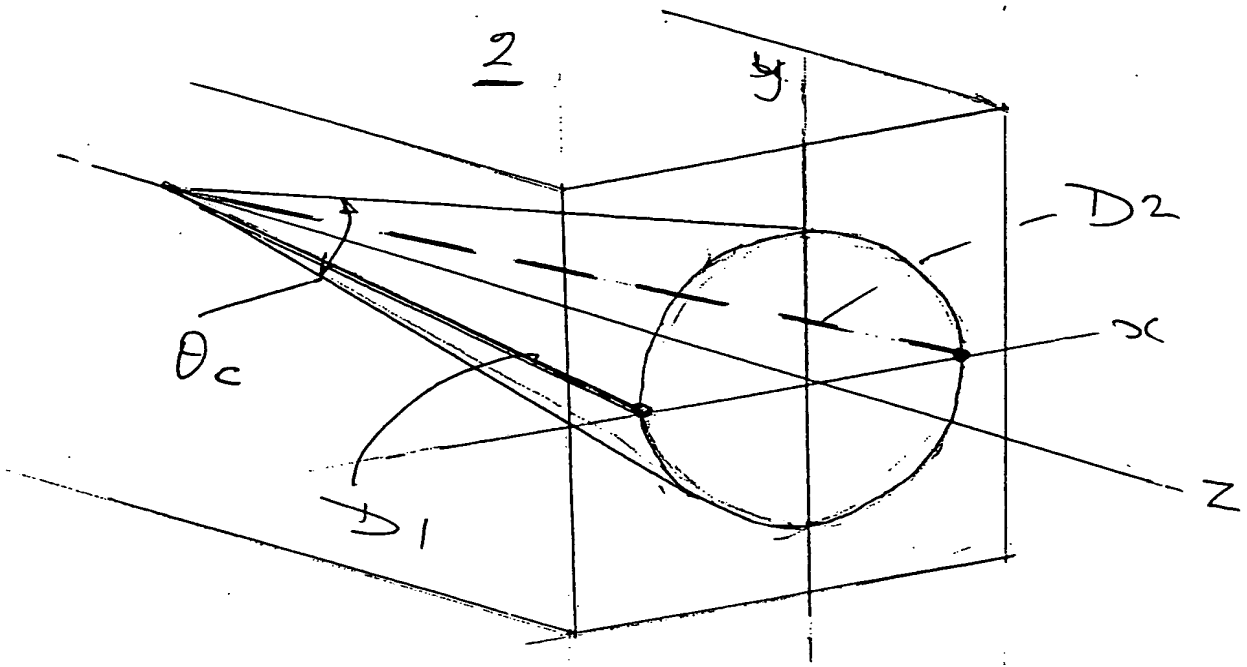
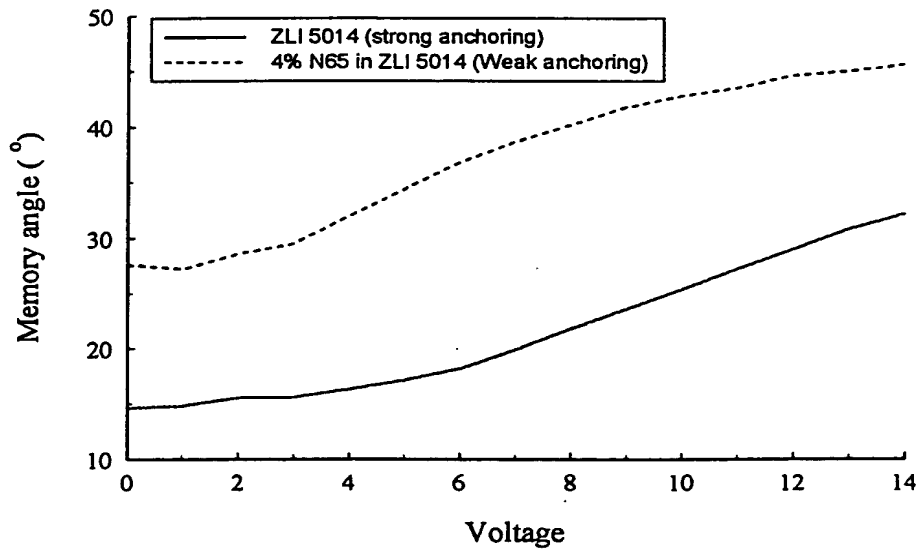


Figure 10 FELCD



PCT / GB 98 / 03011

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